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(54) **A heat mode sensitive imaging element for making positive working printing plates.**

Wärmeempfindliches Aufzeichnungsmaterial für die Herstellung von positiv arbeitenden Druckformen

Matériau d'enregistrement thermosensible pour la fabrication de plaques d'impressions positives

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Description

[0001] The present invention relates to a heat mode imaging element for preparing a lithographic printing plate comprising an IR sensitive top layer.

5 [0002] More specifically the invention is related to a heat mode imaging element for preparing a lithographic printing plate with better physical properties.

BACKGROUND OF THE INVENTION

10 [0003] Lithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

[0004] In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy inks in the photo-exposed (negative-working) or in the non-exposed areas (positive-working) on a hydrophilic background.

15 [0005] In the production of common lithographic printing plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazo-sensitized systems are widely used.

20 [0006] Upon imagewise exposure of the light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.

[0007] Alternatively, printing plates are known that include a photosensitive coating that upon image-wise exposure is rendered soluble at the exposed areas. Subsequent development then removes the exposed areas. A typical example

25 of such photosensitive coating is a quinone-diazide based coating.

[0008] Typically, the above described photographic materials from which the printing plates are made are camera-exposed through a photographic film that contains the image that is to be reproduced in a lithographic printing process. Such method of working is cumbersome and labor intensive. However, on the other hand, the printing plates thus obtained are of superior lithographic quality.

30 [0009] Attempts have thus been made to eliminate the need for a photographic film in the above process and in particular to obtain a printing plate directly from computer data representing the image to be reproduced. However the photosensitive coating is not sensitive enough to be directly exposed with a laser. Therefore it has been proposed to coat a silver halide layer on top of the photosensitive coating. The silver halide may then directly be exposed by means of a laser under the control of a computer. Subsequently, the silver halide layer is developed leaving a silver image on

35 top of the photosensitive coating. That silver image then serves as a mask in an overall exposure of the photosensitive coating. After the overall exposure the silver image is removed and the photosensitive coating is developed. Such method is disclosed in for example JP-A- 60- 61 752 but has the disadvantage that a complex development and associated developing liquids are needed.

[0010] GB-1 492 070 discloses a method wherein a metal layer or a layer containing carbon black is provided on a photosensitive coating. This metal layer is then ablated by means of a laser so that an image mask on the photosensitive layer is obtained. The photosensitive layer is then overall exposed by UV-light through the image mask. After removal of the image mask, the photosensitive layer is developed to obtain a printing plate. This method however still has the disadvantage that the image mask has to be removed prior to development of the photosensitive layer by a cumbersome processing.

45 [0011] Furthermore methods are known for making printing plates involving the use of imaging elements that are heat-sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as described above for making a printing plate is that they have to be shielded from the light. Furthermore they have a problem of sensitivity in view of the storage stability and they show a lower resolution. The trend towards heat mode printing plate precursors is clearly seen on the market.

50 [0012] For example, Research Disclosure no. 33303 of January 1992 discloses a heat mode imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic polymer particles are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink-acceptant without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged

55 since the non-printing areas may become ink accepting when some pressure is applied thereto. Moreover, under critical conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.

[0013] US-P- 4 708 925 discloses imaging elements including a photosensitive composition comprising an alkali-

soluble novolac resin and an onium-salt. This composition may optionally contain an IR-sensitizer. After image-wise exposing said imaging element to UV - visible - or IR-radiation followed by a development step with an aqueous alkali liquid there is obtained a positive or negative working printing plate. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0014] EP-A- 625 728 discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which may be positive or negative working. This layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0015] US-P- 5 340 699 is almost identical with **EP-A- 625 728** but discloses the method for obtaining a negative working IR-laser recording imaging element. The IR-sensitive layer comprises a resole resin, a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

[0016] Furthermore **EP-A- 678 380** discloses a method wherein a protective layer is provided on a grained metal support underlying a laser-ablatable surface layer. Upon image-wise exposure the surface layer is fully ablated as well as some parts of the protective layer. The printing plate is then treated with a cleaning solution to remove the residue of the protective layer and thereby exposing the hydrophilic surface layer.

[0017] EP-A- 97 200 588.8 discloses a heat mode imaging element for making lithographic printing plates comprising on a lithographic base having a hydrophilic surface an intermediate layer comprising a polymer, soluble in an aqueous alkaline solution and a top layer that is sensitive to IR-radiation wherein said top layer upon exposure to IR-radiation has a decreased or increased capacity for being penetrated and/or solubilised by an aqueous alkaline solution.

[0018] EP-A- 97 203 129.8 and **EP-A- 97 203 132.2** disclose a heat mode imaging element consisting of a lithographic base with a hydrophilic surface and a top layer which top layer is sensitive to IR-radiation, comprises a polymer, soluble in an aqueous alkaline solution and is unpenetrable for an alkaline developer containing SiO_2 as silicates

[0019] Said last three heat-mode imaging element have the disadvantage that their physical and chemical resistance is low. Heat mode imaging elements with the convenient processing of said last three heat-mode imaging element but with an improved physical and chemical resistance would be appreciated.

OBJECTS OF THE INVENTION

[0020] It is an object of the invention to provide a heat mode imaging element for making a lithographic printing plate with a wide latitude of development.

[0021] It is an object of the invention to provide a heat mode imaging element for making a lithographic printing plate with a high resolution.

[0022] It is further an object of the present invention to provide a heat mode imaging element for making a lithographic printing plate with improved physical and chemical resistance.

[0023] Further objects of the present invention will become clear from the description hereinafter.

SUMMARY OF THE INVENTION

[0024] According to the present invention there is provided a heat mode imaging element for making a lithographic printing plate comprising on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is IR-sensitive and unpenetrable for an alkaline developer wherein said first layer and said top layer may be one and the same layer; characterized in that said top layer contains at least one compound containing epoxy units in an amount between 20 and 500 mg/m² and a hardener.

DETAILED DESCRIPTION OF THE INVENTION

[0025] The top layer is also called the second layer. The top layer of a heat mode imaging element according to the invention comprises at least one compound containing epoxy units

[0026] As compounds with epoxy units there can be used the technically most important class of epoxy resins. These polymers are produced by the condensation of epichlorohydrin and Bisphenol A or F.

[0027] But there can also be used thermoplast or thermoset modified polymers comprising epoxy-units. Commercially available products are polymers such as epoxy novolac resins, rubber modified epoxy resins, butadiene-acrylonitrile polymer modified epoxy resins, Bisphenol A based polyester resins, epoxidised o-cresylic novolacs, urethane modified epoxy resins, phosphate modified Bisphenol A epoxy resins.

[0028] These polymers can have various molecular weights so that they can be liquid, semi-solid or solid products. Also these products can be used as dispersions in a liquid such as water or another solvent.

[0029] The functionality is a very important parameter in view of the crosslinking behavior. This is expressed as the epoxide equivalent weight (the weight of epoxy functions per molecular weight). This is a measure of the potential crosslink density of the polymer. This epoxide equivalent weight lies preferably between 0.03 and 0.8, more preferably between 0.05 and 0.6.

[0030] The above mentioned epoxy resins can be hardened with a variety of compounds. The most preferred compounds are those belonging to class of the amines, preferably low viscous amines. These can be monomolecular amines, or can also be polymeric products containing amino groups.

[0031] As monomolecular amines can be used amines such as ethylenediamine, diethylenetetramine, dipropylene triamine, monomethanolamine, diethanolamine, triethanolamine, dimethylethanolamine, 2-(2-aminoethoxy)ethanol, morpholine, N-methylmorpholine, N-ethylmorpholine. Also propylamines such as dimethylaminopropylamine, aminopropylmorpholine, methoxypropylamine can be used. Also piperazines like N-aminoethylpiperazine are effective hardening agents. Other suitable amines are cycloaliphatic polyamines such as isophorone diamine, aromatic polyamines or araliphatic polyamines.

[0032] Also suitable amines are polymeric amines.

[0033] A very preferred class of epoxy-hardeners are polyoxyalkyleneamines. These are commercially available as monoamines, diamines and triamines in a great range of molecular weight. The polyether backbone can be based on propylene oxide, ethylene oxide or mixed propylene oxide/ethylene oxide.

[0034] Also preferred hardeners are modified products of basic amines such as polyaminoamides, Mannich bases, polyether modified amines preferably polyether diamines, urethaneamines, polyether urethaneamines, polyamides, dimerized fatty acid-polyamine reaction products.

[0035] 2-Methylimidazole is also preferred as a hardener for compounds with an epoxy function. This results predominantly in the homopolymerization of the epoxy functions. Imidazoles can be used as such or in combination with another amine or hardener. It is preferably used in an amount between 1 to 10 % by mole of the epoxy units

[0036] A trimethylsilane modified polyethyleneimine is also a preferred hardener. Preferably it is used in an amount of 2 to 90 weight percent versus the epoxy content.

[0037] Possibly, the top layer also contains coupling agents. In this case coupling agents are considered as molecules comprising at least two groups with different affinities for the different compounds in the top layer. Typical products are these with an amine or derivative functionality on one side of the molecule and on the other side of the molecule a group capable of absorbing on the carbon black in case of IR-sensibilisation with carbon black. Typical products are trialkylsilanes, aminoalkylsilanes, aminoalkyl-alkoxysilanes such as 3-aminopropyl triethoxysilane, 3-aminopropyl trimethoxysilane and 3-(2-aminoethylamino)-propyl-trimethoxysilane, alkoxysilanes, glycidyl ether alkoxysilanes, alkoxysilane modified polyethyleneamines, modified alkoxysilanes containing mercapto groups and isocyanatoalkyl trialkoxysilanes. These coupling agents are preferably used in an amount of 5 to 30 mole percent versus the epoxy content.

[0038] In a first embodiment the first layer and the top layer are different. In said embodiment there is provided a heat mode imaging element for making lithographic printing plates having on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is sensitive to IR-radiation and which is unpenetrable for an alkaline developer.

[0039] The top layer, in accordance with the present invention comprises an IR-dye or pigment and a binder resin. A mixture of IR-dyes or pigments may be used, but it is preferred to use only one IR-dye or pigment. Preferably said IR-dyes are IR-cyanine dyes. Particularly useful IR-cyanine dyes are cyanine dyes with two indolenine groups.

[0040] Particularly useful IR-absorbing pigments are carbon black, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. WO2.9. It is also possible to use conductive polymer dispersion such as polypyrrole or polyaniline-based conductive polymer dispersions. The lithographic performance and in particular the print endurance obtained depends on the heat-sensitivity of the imaging element. In this respect it has been found that carbon black yields very good and favorable results.

[0041] The IR-absorbing dyes or pigments are present preferably in an amount between 1 and 99 parts, more preferably between 50 and 95 parts by weight of the total amount of said IR-sensitive top layer.

[0042] The top layer may preferably comprise as binder a water insoluble polymer such as a cellulose ester, a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, silicone resins, etc. Preferred as binder is nitrocellulose resin.

[0043] The total amount of the top layer preferably ranges from 0.05 to 10 g/m², more preferably from 0.1 to 2 g/m².

[0044] In the top layer a difference in the capacity of being penetrated and/or solubilised by the aqueous alkaline solution is generated upon image-wise exposure for an alkaline developer according to the invention.

[0045] In the present invention the said capacity is increased upon image-wise IR exposure to such degree that the imaged parts will be cleaned out during development without solubilising and/or damaging the non-imaged parts.

[0046] The development with the aqueous alkaline solution is preferably done within an interval of 5 to 120 seconds.

[0047] Between the top layer and the lithographic base the present invention comprises a first layer soluble in an

aqueous alkaline developing solution with preferentially a pH between 7.5 and 14. Said layer is preferably contiguous to the top layer but other layers may be present between the top layer and the first layer. The alkali soluble binders used in this layer are preferably hydrophobic binders as used in conventional positive or negative working PS-plates e.g. novolac polymers, polymers containing hydroxystyrene units, carboxy substituted polymers etc. Typical examples of these polymers are described in **DE-A- 4 007 428**, **DE-A- 4 027 301** and **DE-A- 4 445 820**. The hydrophobic binder used in connection with the present invention is further characterised by insolubility in water and partial solubility/swellability in an alkaline solution and/or partial solubility in water when combined with a cosolvent.

[0048] Furthermore this aqueous alkali soluble layer is preferably a visible light- and UV-light desensitised layer. Said layer is preferably thermally hardenable. This preferably visible light- and UV-desensitised layer does not comprise photosensitive ingredients such as diazo compounds, photoacids, photoinitiators, quinone diazides, sensitisers etc. which absorb in the wavelength range of 250nm to 650nm. In this way a daylight stable printing plate may be obtained.

[0049] Said first layer preferably also includes a low molecular acid, preferably a carboxylic acid, still more preferably a benzoic acid, most preferably 3,4,5-trimethoxybenzoic acid or a benzophenone.

[0050] The ratio between the total amount of low molecular acid or benzophenone and polymer in the first layer preferably ranges from 2:98 to 40:60, more preferably from 5:95 to 20:80. The total amount of said first layer preferably ranges from 0.1 to 10 g/m², more preferably from 0.3 to 2 g/m².

[0051] The first layer and/or the top (also called the second) layer preferably comprises a surfactant. Said surfactant can be a cationic, an anionic or an amphoteric surfactant, but is more preferably a non-ionic surfactant. The surfactant is most preferably selected from the group consisting of perfluoroalkyl surfactants, alkylphenyl surfactants and particularly preferably polyether-modified polysiloxane surfactants. The surfactant is preferably present in the top layer. The amount of surfactant lies preferably in the range from 0.001 to 0.3g/m², more preferably in the range from 0.003 to 0.050g/m².

[0052] In the imaging element according to the present invention, the lithographic base may be an anodised aluminum for all embodiments. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. The anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or may be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution.

Still further, the aluminum oxide surface may be treated with polyvinylphosphonic acid, polyvinylmethylphosphonic acid, phosphoric acid esters of polyvinyl alcohol, polyvinylsulphonic acid, polyvinylbenzenesulphonic acid, sulphuric acid esters of polyvinyl alcohol, and acetals of polyvinyl alcohols formed by reaction with a sulphonated aliphatic aldehyde. It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in **GB-A- 1 084 070**, **DE-A- 4 423 140**, **DE-A- 4 417 907**, **EP-A- 659 909**, **EP-A- 537 633**, **DE-A- 4 001 466**, **EP-A- 292 801**, **EP-A- 291 760** and **US-P- 4 458 005**.

[0053] According to another mode in connection with the present invention, the lithographic base having a hydrophilic surface comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer for all embodiments. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetra-alkylorthosilicate. The latter is particularly preferred.

[0054] As hydrophilic binder there may be used hydrophilic (co)polymers such as for example, homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylate acid, methacrylate acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

[0055] The amount of crosslinking agent, in particular of tetraalkyl orthosilicate, is preferably at least 0.2 parts by weight per part by weight of hydrophilic binder, more preferably between 0.5 and 5 parts by weight, most preferably between 1.0 parts by weight and 3 parts by weight.

[0056] A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert particles of larger size than the colloidal silica may be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and

valleys, which serve as storage places for water in background areas.

[0057] The thickness of a cross-linked hydrophilic layer in a lithographic base in accordance with this embodiment may vary in the range of 0.2 to 25 μm and is preferably 1 to 10 μm .

5 [0058] Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention are disclosed in EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, US-P- 4 284 705 and EP-A- 514 490.

[0059] As flexible support of a lithographic base in connection with the present embodiment it is particularly preferred to use a plastic film e.g. substrated polyethylene terephthalate film, substrated polyethylene naphthalate film, cellulose acetate film, polystyrene film, polycarbonate film etc... The plastic film support may be opaque or transparent.

10 [0060] It is particularly preferred to use a polyester film support to which an adhesion improving layer has been provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in EP-A- 619 524, EP-A- 620 502 and EP-A- 619 525. Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2 . Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

15 [0061] In a second embodiment the first layer and the second layer are the same. In said embodiment there is provided a heat mode imaging element for making lithographic printing plates having on a lithographic base with a hydrophilic surface a top layer which top layer is sensitive to IR-radiation, comprises a polymer, soluble in an aqueous alkaline solution and is unpenetrable for an alkaline developer.

20 [0062] The IR-sensitive layer, in accordance with the present invention comprises an IR-dye or pigment and a polymer, soluble in an aqueous alkaline solution. A mixture of IR-dyes or pigments may be used, but it is preferred to use only one IR-dye or pigment. Suitable IR-dyes and pigments are those mentioned above in the first embodiment of the present invention.

25 [0063] The IR-dyes or pigments are present preferably in an amount between 1 and 60 parts, more preferably between 3 and 50 parts by weight of the total amount of said IR-sensitive top layer.

[0064] The alkali soluble polymers used in this layer are preferably hydrophobic and ink accepting polymers as used in conventional positive or negative working PS-plates e.g. carboxy substituted polymers etc. More preferably is a phenolic resin such as a hydroxystyrene units containing polymer or a novolac polymer. Most preferred is a novolac polymer. Typical examples of these polymers are described in DE-A- 4 007 428, DE-A- 4 027 301 and DE-A- 4 445 30 820. The hydrophobic polymer used in connection with the present invention is further characterised by insolubility in water and at least partial solubility/swellability in an alkaline solution and/or at least partial solubility in water when combined with a cosolvent.

[0065] Furthermore this IR-sensitive layer is preferably a visible light- and UV-light desensitised layer. Still further said layer is preferably thermally hardenable. This preferably visible light- and UV-light desensitised layer does not 35 comprise photosensitive ingredients such as diazo compounds, photoacids, photoinitiators, quinone diazides, sensitizers etc. which absorb in the wavelength range of 250nm to 650nm. In this way a daylight stable printing plate may be obtained.

[0066] Said IR-sensitive layer preferably also includes a low molecular acid, more preferably a carboxylic acid, still more preferably a benzoic acid, most preferably 3,4,5-trimethoxybenzoic acid or a benzofenone, more preferably tri- 40 hydroxybenzofenone.

[0067] The ratio between the total amount of low molecular acid or benzofenone and polymer in the IR-sensitive layer preferably ranges from 2:98 to 40:60, more preferably from 5:95 to 30:70. The total amount of said IR-sensitive layer preferably ranges from 0.1 to 10 g/m^2 , more preferably from 0.3 to 2 g/m^2 .

45 [0068] The top layer preferably comprises a surfactant. Said surfactant can be a cationic, an anionic or an amphoteric surfactant, but is more preferably a non-ionic surfactant. The surfactant is most preferably selected from the group consisting of perfluoroalkyl surfactants, alkylphenyl surfactants and particularly preferably polysiloxane surfactants such as polysiloxane polyethers, polysiloxane copolymers, alkyl-aryl modified methyl-polysiloxanes and acylated polysiloxanes. The amount of surfactant lies preferably in the range from 0.001 to 0.3 g/m^2 , more preferably in the range from 0.003 to 0.050 g/m^2 .

50 [0069] In the IR-sensitive layer a difference in the capacity of being penetrated and/or solubilised by the alkaline developer is generated upon image-wise exposure for an alkaline developer according to the invention.

[0070] To prepare a lithographic plate, the heat-mode imaging element is image-wise exposed and developed.

55 [0071] Image-wise exposure in connection with the present invention is an image-wise scanning exposure involving the use of a laser that operates in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared. Exposure of the imaging element may be performed with lasers with a short as well as with lasers with a long pixel dwell time. Preferred are lasers with a pixel dwell time between 0.005 μs and 20 μs .

[0072] After the image-wise exposure the heat mode imaging element is developed by rinsing it with an aqueous

alkaline solution. The aqueous alkaline solutions used in the present invention are those that are used for developing conventional positive working sensitized printing plates, preferably containing SiO_2 as silicates and having preferably a pH between 11.5 and 14. Thus the imaged parts of the top layer that will be rendered more penetrable for the aqueous alkaline solution upon exposure are cleaned-out whereby a positive working printing plate is obtained.

[0073] In the present invention, the composition of the developer used is also very important.

[0074] Therefore, to perform development processing stably for a long time period particularly important are qualities such as strength of alkali and the concentration of silicates in the developer. Under such circumstances, the present inventors have found that a rapid high temperature processing can be performed, that the amount of the replenisher to be supplemented is low and that a stable development processing can be performed over a long time period of the order of not less than 3 months without exchanging the developer only when the developer having the foregoing composition is used.

[0075] The developers and replenishers for developer used in the invention are preferably aqueous solutions mainly composed of alkali metal silicates and alkali metal hydroxides represented by MOH or their oxide, represented by M_2O , wherein said developer comprises SiO_2 and M_2O in a molar ratio of 0.5 to 1.5 and a concentration of SiO_2 of 0.5 to 5% by weight. As such alkali metal silicates, preferably used are, for instance, sodium silicate, potassium silicate, lithium silicate and sodium metasilicate. On the other hand, as such alkali metal hydroxides, preferred are sodium hydroxide, potassium hydroxide and lithium hydroxide.

[0076] The developers used in the invention may simultaneously contain other alkaline agents. Examples of such other alkaline agents include such inorganic alkaline agents as ammonium hydroxide, sodium tertiary phosphate, sodium secondary phosphate, potassium tertiary phosphate, potassium secondary phosphate, ammonium tertiary phosphate, ammonium secondary phosphate, sodium bicarbonate, sodium carbonate, potassium carbonate and ammonium carbonate; and such organic alkaline agents as mono-, di- or triethanolamine, mono-, di- or trimethylamine, mono-, di- or triethylamine, mono- or diisopropylamine, n-butylamine, mono-, di- or triisopropanolamine, ethyleneimine, ethylenediimine and tetramethylammonium hydroxide.

[0077] In the present invention, particularly important is the molar ratio in the developer of $[\text{SiO}_2] / [\text{M}_2\text{O}]$, which is generally 0.6 to 1.5, preferably 0.7 to 1.3. This is because if the molar ratio is less than 0.6, great scattering of activity is observed, while if it exceeds 1.5, it becomes difficult to perform rapid development and the dissolving out or removal of the light-sensitive layer on non-image areas is liable to be incomplete. In addition, the concentration of SiO_2 in the developer and replenisher preferably ranges from 1 to 4 % by weight. Such limitation of the concentration of SiO_2 makes it possible to stably provide lithographic printing plates having good finishing qualities even when a large amount of plates according to the invention are processed for a long time period.

[0078] In a particular preferred embodiment, an aqueous solution of an alkali metal silicate having a molar ratio $[\text{SiO}_2] / [\text{M}_2\text{O}]$, which ranges from 1.0 to 1.5 and a concentration of SiO_2 of 1 to 4 % by weight is used as a developer. In such case, it is a matter of course that a replenisher having alkali strength equal to or more than that of the developer is employed. In order to decrease the amount of the replenisher to be supplied, it is advantageous that a molar ratio, $[\text{SiO}_2] / [\text{M}_2\text{O}]$, of the replenisher is equal to or smaller than that of the developer, or that a concentration of SiO_2 is high if the molar ratio of the developer is equal to that of the replenisher.

[0079] In the developers and the replenishers used in the invention, it is possible to simultaneously use organic solvents having solubility in water at 20 °C of not more than 10 % by weight according to need. Examples of such organic solvents are such carboxylic acid esters as ethyl acetate, propyl acetate, butyl acetate, amyl acetate, benzyl acetate, ethylene glycol monobutyl acetate, butyl lactate and butyl levulinate; such ketones as ethyl butyl ketone, methyl isobutyl ketone and cyclohexanone; such alcohols as ethylene glycol monobutyl ether, ethylene glycol benzyl ether, ethylene glycol monophenyl ether, benzyl alcohol, methylphenylcarbinol, n-amyl alcohol and methylamyl alcohol; such alkyl-substituted aromatic hydrocarbons as xylene; and such halogenated hydrocarbons as methylene dichloride and monochlorobenzene. These organic solvents may be used alone or in combination. Particularly preferred is benzyl alcohol in the invention. These organic solvents are added to the developer or replenisher therefor generally in an amount of not more than 5 % by weight and preferably not more than 4 % by weight.

[0080] The developers and replenishers used in the present invention may simultaneously contain a surfactant for the purpose of improving developing properties thereof. Examples of such surfactants include salts of higher alcohol ($\text{C}_8 \sim \text{C}_{22}$) sulfuric acid esters such as sodium salt of lauryl alcohol sulfate, sodium salt of octyl alcohol sulfate, ammonium salt of lauryl alcohol sulfate, Teepol B-81 (trade mark, available from Shell Chemicals Co., Ltd.) and disodium alkyl sulfates; salts of aliphatic alcohol phosphoric acid esters such as sodium salt of cetyl alcohol phosphate; alkyl aryl sulfonic acid salts such as sodium salt of dodecylbenzene sulfonate, sodium salt of isopropyl naphthalene sulfonate, sodium salt of dinaphthalene disulfonate and sodium salt of metanitrobenzene sulfonate; sulfonic acid salts of alkylamides such as $\text{C}_{17}\text{H}_{33}\text{CON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$ and sulfonic acid salts of dibasic aliphatic acid esters such as sodium dioctyl sulfosuccinate and sodium dihexyl sulfosuccinate. These surfactants may be used alone or in combination. Particularly preferred are sulfonic acid salts. These surfactants may be used in an amount of generally not more than 5 % by weight and preferably not more than 3 % by weight.

[0081] In order to enhance developing stability of the developers and replenishers used in the invention, the following compounds may simultaneously be used.

[0082] Examples of such compounds are neutral salts such as NaCl, KCl and KBr as disclosed in JN-A- 58- 75 152; chelating agents such as EDTA and NTA as disclosed in JN-A- 58- 190 952 (U.S-A- 4 469 776), complexes such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ as disclosed in JN-A- 59- 121 336 (US-A- 4 606 995); ionizable compounds of elements of the group IIa, IIIa or IIIb of the Periodic Table such as those disclosed in JN-A- 55- 25 100; anionic or amphoteric surfactants such as sodium alkyl naphthalene sulfonate and N-tetradecyl-N,N-dihydroxyethyl betaine as disclosed in JN-A- 50- 51 324; tetramethyldecyne diol as disclosed in US-A- 4 374 920; non-ionic surfactants as disclosed in JN-A- 60- 213 943; cationic polymers such as methyl chloride quaternary products of p-dimethylaminomethyl polystyrene as disclosed in JN-A- 55- 95 946; amphoteric polyelectrolytes such as copolymer of vinylbenzyl trimethylammonium chloride and sodium acrylate as disclosed in JN-A- 56- 142 528; reducing inorganic salts such as sodium sulfite as disclosed in JN-A- 57- 192 952 (US-A- 4 467 027) and alkaline-soluble mercapto compounds or thioether compounds such as thiosalicylic acid, cysteine and thioglycolic acid; inorganic lithium compounds such as lithium chloride as disclosed in JN-A- 58- 59 444; organic lithium compounds such as lithium benzoate as disclosed in JN-A- 50 34 442; organometallic surfactants containing Si, Ti or the like as disclosed in JN-A- 59- 75 255; organoboron compounds as disclosed in JN-A- 59- 84 241 (US-A- 4 500 625); quaternary ammonium salts such as tetraalkylammonium oxides as disclosed in EP-A- 101 010; and bactericides such as sodium dehydroacetate as disclosed in JN-A- 63- 226 657.

[0083] In the method for development processing of the present invention, any known means of supplementing a replenisher for developer may be employed. Examples of such methods preferably used are a method for intermittently or continuously supplementing a replenisher as a function of the amount of PS plates processed and time as disclosed in JN-A- 55- 115 039 (GB-A- 2 046 931), a method comprising disposing a sensor for detecting the degree of light-sensitive layer dissolved out in the middle portion of a developing zone and supplementing the replenisher in proportion to the detected degree of the light-sensitive layer dissolved out as disclosed in JN-A- 58- 95 349 (US-A- 4 537 496); a method comprising determining the impedance value of a developer and processing the detected impedance value by a computer to perform supplementation of a replenisher as disclosed in GB-A- 2 208 249.

[0084] The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate is soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder is slid on the print cylinder instead of applying in a classical way a classically formed printing plate. More details on sleeves are given in "Grafisch Nieuws" ed. Keesing, 15, 1995, page 4 to 6.

[0085] After the development of an image-wise exposed imaging element with an aqueous alkaline solution and drying, the obtained plate can be used as a printing plate as such. However, to improve durability it is still possible to bake said plate at a temperature between 200°C and 300°C for a period of 30 seconds to 5 minutes. Also the imaging element can be subjected to an overall post-exposure to UV-radiation to harden the image in order to increase the run length of the printing plate.

[0086] The following examples illustrate the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

EXAMPLE 1 (Comparative example)

Preparation of the lithographic base

[0087] A 0.30 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m² to form a surface topography with an average center-line roughness Ra of 0.5 µm.

[0088] After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized water at 25°C for 30 seconds.

[0089] The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m² for about 300 seconds to form an anodic oxidation film of 3.00 g/m² of Al₂O₃ then washed with demineralized water, posttreated with a solution containing polyvinylphosphonic acid and subsequently with a solution containing aluminum trichloride, rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the heat-mode imaging element

[0090] On the above described lithographic base was first coated a layer from a 8.6% wt solution in tetrahydrofuran/

methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM (sold by Clariant, Germany) and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 0.735% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM (both dispersing agents of Zeneca specialities, G.B.), 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM (both polysiloxane surfactants of Tego, Germany).

EXAMPLE 2 (Comparative example)

[0091] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0092] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 0.2720% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 35 mg/m² of IR-absorber ST798 TM: 2-(2-(2-Chloro-3-(2-dihydro-1,1,3-trimethyl-2H-benzo(e)indole-2-ylidene)-ethylidene)-1-cyclohexen-1-yl)-ethenyl)-1,1,3-trimethyl-1H-benzo(e)indolium 4-methylbenzenesulfonate, 12.4 mg/m² of FLEXO-BLAU 630 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

ST798 is commercially available by Synthron Wolfen Germany, FLEXO-BLAU 630 is commercially available by BASF, Ludwigshafen, Germany.

EXAMPLE 3

[0093] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0094] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 25.2 mg/m² of EPI-REZ 3510 W-60 TM, 29.8 mg/m² of TB 3354H TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. TB 3354H is an aminehardener for water soluble epoxies, commercially available at Witco GmbH.

EXAMPLE 4

[0095] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0096] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 25.0 mg/m² of EPI-REZ 3510 W-60 TM, 30.0 mg/m² of EUREDUR 115 TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. EUREDUR 115 is a polyamidoamino, commercially available at Witco GmbH.

EXAMPLE 5

[0097] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0098] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 25.8 mg/m² of EPI-REZ 3510 W-60 TM, 29.2 mg/m² of JEFFAMINE ED900 TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. JEFFAMINE ED900 is a polyetherdiamine which is based on a predominately polyethyleneoxide backbone, commercially available at Huntsman Corporation, Houston.

EXAMPLE 6

[0099] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0100] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 22.7 mg/m² of EPI-REZ 6006 W-70 TM, 32.3 mg/m² of TB 3354H TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 6006 W-70 is an epoxidised o-cresolnovolac resin, commercially available at Shell Chemicals. TB 3354H is an aminehardener for water soluble epoxies, commercially available at Witco GmbH.

EXAMPLE 7

[0101] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0102] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 32.2 mg/m² of EPI-REZ 5520 W-60 TM, 22.8 mg/m² of TB 3354H TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 5520 W-60 is an urethane modified epoxy resin, commercially available at Shell Chemicals. TB 3354H is an aminehardener for water soluble epoxies, commercially available at Witco GmbH.

EXAMPLE 8

[0103] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0104] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 6.5 mg/m² of EPI-REZ 3510 W-60 TM, 48.5 mg/m² of JEFFAMINE M3003 TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. JEFFAMINE M3003 is a monoamine with a propyleneoxide/ethyleneoxide ratio of 8/49 and molecular weight about 3000, commercially available at Huntsman Corporation, Houston.

EXAMPLE 9

[0105] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0106] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 37.2 mg/m² of EPI-REZ 3510 W-60 TM, 17.8 mg/m² of EPI-CURE 3140 TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. EPI-CURE 3140 is a low viscosity polyamide, also commercially available at Shell Chemicals.

EXAMPLE 10

[0107] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0108] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 52.4 mg/m² of EPI-REZ 3510 W-60 TM, 2.6 mg/m² of poly(ethyleneimine) substituted trimethoxysilyl propyl, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. Poly(ethyleneimine) substituted trimethoxysilyl propyl is commercially available at ABCR.

EXAMPLE 11

[0109] The same base was used as described in comparative example 1.

5 Preparation of the heat-mode imaging element

[0110] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

10 Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 31.4 mg/m² of EPI-REZ 3510 W-60 TM, 23.6 mg/m² of JEFFAMINE T403 TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000TM, 2.0 mg/m² of TEGO WST 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

15 EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. JEFFAMINE T403 is a trifunctional propyleneoxide amine, commercially available at Witco GmbH.

EXAMPLE 12

20

[0111] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

25 [0112] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

30 Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.2345% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 95.2 mg/m² of EPI-REZ 3510 W-60 TM, 4.8 mg/m² of 2-methylimidazole, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of Tego Wet 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

35 EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. For 2-methylimidazole, a 99% grade was used, commercially available at Aldrich Chemie.

EXAMPLE 13

40 [0113] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

45 [0114] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

50 The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 22.9 mg/m² of EPI-REZ 3510 W-60 TM, 27.5 mg/m² of EUREDUR 115 TM, 4.6 mg/m² of 3-aminopropyltriethoxysilane, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

For the preparation of the coating solution, it is very important to add first of all the 3-aminopropyltriethoxysilane to the dispersion before adding the epoxy resin or hardener.

55 EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. EUREDUR 115 is a polyamidoamino, commercially available at Witco GmbH. For the 3-aminopropyltriethoxysilane a 98% purity grade from Aldrich Chemie Steinheim was used.

EXAMPLE 14

[0115] The same base was used as described in comparative example 1.

5 Preparation of the heat-mode imaging element

[0116] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

10 Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 36.2 mg/m² of EUREPOX 7001/75W TM, 9.4 mg/m² of EUREDUR 115 TM, 9.4 mg/m² of 3-(2-aminoethyl amino)-propyl-trimethoxysilane, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

For the preparation of the coating solution, it is very important to add first of all the 3-(2-aminoethyl amino)-propyl-trimethoxysilane to the dispersion before adding the epoxy resin or hardener.

20 EUREPOX 7001/75W is a Bisphenol A - epoxy resin, commercially available by Witco GmbH. EUREDUR 115 is a polyamidoamino, commercially available at Witco GmbH. For 3-(2-aminoethyl amino)-propyl-trimethoxysilane, KBM-603 from Shin Etsu Chemicals Co, Ltd was used.

EXAMPLE 15

25 [0117] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

30 [0118] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in Tetrahydrofuran/Methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 1.0095% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

35 The resulting IR-sensitive layer contained 115 mg/m² of carbon black, 36.2 mg/m² of EUREPOX 7001/75W TM, 9.4 mg/m² of EUREDUR 115 TM, 9.4 mg/m² of DYNASILAN AMMO TM, 11.5 mg/m² of nitrocellulose, 2.1 mg/m² of SOLSPERSE 5000 TM, 11.3 mg/m² of SOLSPERSE 28000 TM, 2.0 mg/m² of Tego Wet 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

40 For the preparation of the coating solution, it's very important to add first of all the DYNASILAN AMMO: 3-aminopropyl trimethoxysilane to the dispersion before adding the epoxy resin or hardener.

EUREPOX 7001/75W is a Bisphenol A - epoxy resin, commercially available by Witco GmbH. EUREDUR 115 is a polyamidoamino, commercially available at Witco GmbH. DYNASILAN AMMO is a commercial product of Hills AG.

EXAMPLE 16

45

[0119] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

50 [0120] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

55 Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 0.4220% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds. The resulting IR-sensitive layer contained 35 mg/m² of IR-absorber ST798 TM: 2-(2-(2-Chloro-3-(2-dihydro-1,1,3-trimethyl-2H-benzo(e)indole-2-ylidene)-ethylidene)-1-cyclohexen-1-yl)-ethenyl)-1,1,3-trimethyl-1H-benzo(e)indolium 4-methylbenzenesulfonate, 12.4 mg/m² of FLEXO-BLAU 630 TM, 13.8 mg/m² of EPI-REZ 3510 W-60 TM, 16.2 mg/m² of TB 3354H TM, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM.

ST798 is commercially available by Synthron Wolfen Germany, FLEXO-BLAU 630 is commercially available by BASF, Ludwigshafen, Germany. EPI-REZ 3510 W-60 is a waterborne dispersion of a liquid Bisphenol A epoxy resin, commercially available at Shell Chemicals. TB 3354H is an aminehardener for water soluble epoxies, commercially available at Witco GmbH.

EXAMPLE 17

[0121] The same base was used as described in comparative example 1.

Preparation of the heat-mode imaging element

[0122] On the lithographic base described in example 1, was first coated a layer from an 8.6% wt solution in tetrahydrofuran/methoxypropanol 55/45 ratio, with a wet coating thickness of 14µm. The resulting layer contained 88% of ALNOVOL SPN452 TM and 12% of 3,4,5-trimethoxybenzoic acid.

Upon this layer was coated with a wet coating thickness of 20µm, the IR-sensitive layer from a 0.4220% wt solution in methylethylketone/methoxypropanol 50/50 ratio. This layer was dried on a temperature of at least 120°C for at least 40 seconds.

The resulting IR-sensitive layer contained 35 mg/m² of IR-absorber ST798 TM: 2-(2-(2-Chloro-3-(2-dihydro-1,1,3-trimethyl-2H-benzo(e)indole-2-ylidene)-ethylidene)-1-cyclohexen-1-yl)-ethenyl)-1,1,3-trimethyl-1H-benzo(e)indolium 4-methylbenzenesulfonate, 12.4 mg/m² of FLEXO-BLAU 630 TM, 22.7 mg/m² of EUREPOX 7001/75W TM, 3.6 mg/m² of EUREDUR 115 TM, 3.6 mg/m² of 3-aminopropyltriethoxysilane, 2.0 mg/m² of TEGO WET 265 TM and 5.0 mg/m² of TEGO GLIDE 410 TM. ST798 is commercially available by Synthron Wolfen Germany, FLEXO-BIAU 630 is commercially available by BASF, Ludwigshafen, Germany. EUREPOX 7001/75W is a Bisphenol A - epoxy resin, commercially available by Witco GmbH. EUREDUR 115 is a polyamidoamino, commercially available at Witco GmbH. For the 3-aminopropyltriethoxysilane a 98% purity grade from Aldrich Chemie Steinheim was used.

Scratching the heat-mode imaging element

[0123] The above mentioned materials in comparative example 1 and examples 2 till 17 were scratched in a standard test. In this test scratches are formed by displacing needles at a speed of 96 cm/min, under well defined loads. The needles are of type robin with a radius of 1.5 mm. 15 scratches are formed under following loads: 57 - 85 - 114 - 142 - 170 - 113 - 169 - 225 - 282 - 338 - 400 - 600 - 800 - 1000 en 1200 mN.

After creation of the 15 scratches the material was exposed.

Exposing the heat-mode imaging element

[0124] All the above mentioned materials were imaged with a Creo 3244TTM external drum platesetter at 263 mJ/cm² and 2400 dpi.

Developing the imagewise exposed element

[0125] After exposure of prepared imaging element, the element was developed in an aqueous alkaline developing solution. These developing was carried out in a Technigraph NPX-32 processor at a speed of 1 m/min at 25°C, filled with OZASOL EP262A TM (OZASOL EP262A is commercially available from Agfa) and with water in the rinsing section and OZASOL RC795 TM gum in the gumming section.

Testing chemical resistance

[0126] On the image plane and on the screen plane, a drop of 40µl of a 30% solution of iso-propanol/water mixture is placed. After 10 minutes the drop is taken away by means of a cotton pad. This is repeated with a 40 and a 50% mixture of iso-propanol in water.

Evaluation of lithographic quality of the material

[0127] The plates are printed on a Heidelberg GTO46 printing machine with a conventional ink (K+E) and fountain solution (Rotamatic). The prints are evaluated on scumming in the IR-exposed areas and on good ink-uptake in the non-imaged areas.

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Evaluation of the scratch resistance on the prints

[0128] The 15 scratches are controlled on width of damage and given a corresponding quotation as indicated in table 1.

Table 1:

Quotation	Width of scratch
0	no scratch visible
1	scratch smaller than 50µm
2	width between 50 and 100 µm
3	width between 100 and 150 µm
4	width between 150 and 200 µm
5	width greater than 200 µm

A summation of all given quotations results in the scratch resistance of the material. The lower the value, the better the scratch resistance.

Evaluation of the chemical resistance

[0129] On the prints, the six places where the drops were located are visually controlled on damage of the image. No attack is given a quotation of 0. Total disappearance of the image is given a quotation of 4. All the six quotations are summated resulting in a figure for chemical resistance. This delivers a value between 0 and 24. A higher value means a reduced chemical resistance.

Results

[0130]

Example	scratch resistance	Chemical resistance	Print quality
Comp 1	27	20	OK
Ex 3	10	9	OK
Ex 4	10	15	OK
Ex 5	14	11	OK
Ex 6	16	8	OK
Ex 7	12	14	OK
Ex 8	6	10	OK
Ex 9	14	9	OK
Ex 10	8	15	OK
Ex 11	20	2	OK
Ex 12	18	14	OK
Ex 13	7	15	OK
Ex 14	19	9	OK
Ex 15	19	15	OK
Comp 2	19	15	OK
Ex 16	14	14	OK
Ex 17	13	15	OK

Print quality OK means: no visible scumming on non-image parts and good ink-uptake.

[0131] It is clear from the results of table 2 that all the examples according to the invention have a better scratch resistance than the comparative examples and that the examples according to the invention which contain carbon black as IR-absorber have a better chemical resistance than the corresponding comparative example.

Claims

1. A heat mode imaging element for making a lithographic printing plate comprising on a lithographic base with a hydrophilic surface a first layer including a polymer, soluble in an aqueous alkaline solution and a top layer on the same side of the lithographic base as the first layer which top layer is IR-sensitive and unpenetrable for an alkaline developer wherein said first layer and said top layer may be one and the same layer; **characterized in that** said top layer contains at least one compound containing epoxy units in an amount between 20 and 500 mg/m² and a hardener.
2. A heat mode imaging element according to claim 1 wherein said compound containing epoxy units is a condensation product of epichlorohydrine and Bisphenol A.
3. A heat mode imaging element according to claim 1 wherein said compound containing epoxy units is a compound selected from the group consisting of epoxydized o-cresol novolac resins and urethane modified epoxy resins.
4. A heat mode imaging element according to any of claims 1 to 3 wherein said top layer comprises a low viscous amine as hardener.
5. A heat mode imaging element according to any of claims 1 to 3 wherein said top layer comprises a compound selected from the group consisting of polyaminoamides and polyamides as hardener.
6. A heat mode imaging element according to any of claims 1 to 3 wherein said top layer comprises a compound selected from the group of monoamine polyoxyalkyleneamines, diamine polyoxyalkyleneamines and triamine polyoxyalkyleneamines as hardeners.
7. A heat mode imaging element according to any of claims 1 to 3 wherein said top layer comprises a trimethylsilane modified polyethyleneimine as hardener.
8. A heat mode imaging element according to any of claims 1 to 4 wherein said top layer comprises 2-methylimidazole as hardener.
9. A heat mode imaging element according to any of claims 1 to 8 wherein said top layer comprises an aminoalkyl trialkoxysilane as coupling agent.
10. A method for making a lithographic printing plate comprising the steps of
 - a) exposing imagewise to IR-radiation a heat mode imaging element according to any of claims 1 to 9; and
 - b) developing said imagewise exposed heat mode imaging element with an aqueous alkaline developer whereby the exposed areas of the first and the top layer, which may be the same, are dissolved and the unexposed areas of the first layer remain undissolved.

Patentansprüche

1. Ein wärmeempfindliches Bilderzeugungselement zur Herstellung einer lithografischen Druckplatte, wobei das Bilderzeugungselement auf einer lithografischen Unterlage mit einer hydrophilen Oberfläche eine erste Schicht mit einem in einer wäßrig-alkalischen Lösung löslichen Polymer und auf der gleichen Seite der lithografischen Unterlage wie die erste Schicht eine Deckschicht enthält, die empfindlich gegenüber Infrarotstrahlung und undurchdringbar für einen alkalischen Entwickler ist, wobei die erste Schicht und die Deckschicht ein und dieselbe Schicht sein können, **dadurch gekennzeichnet, daß** die Deckschicht zumindest eine Epoxideinheiten und einen Härter enthaltende Verbindung in einer Menge zwischen 20 und 500 mg/m² enthält.

2. Ein wärmeempfindliches Bilderzeugungselement nach Anspruch 1, **dadurch gekennzeichnet, daß** die Epoxid-einheiten enthaltende Verbindung ein Kondensationsprodukt von Epichlorhydrin und Bisphenol A ist.
- 5 3. Ein wärmeempfindliches Bilderzeugungselement nach Anspruch 1, **dadurch gekennzeichnet, daß** die Epoxid-einheiten enthaltende Verbindung eine Verbindung aus der Gruppe bestehend aus epoxidierten o-Kresol-Novolak-Harzen und urethanmodifizierten Epoxyharzen ist.
- 10 4. Ein wärmeempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** die Deckschicht ein niederviskoses Amin als Härter enthält.
- 15 5. Ein wärmeempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** die Deckschicht als Härter eine Verbindung aus der Gruppe bestehend aus Polyaminoamiden und Polyamiden enthält.
- 20 6. Ein wärmeempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** die Deckschicht als Härter eine Verbindung aus der Gruppe bestehend aus Monoaminpolyoxyalkylenaminen, Diaminpolyoxyalkylenaminen und Triaminpolyoxyalkylenaminen enthält.
- 25 7. Ein wärmeempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** die Deckschicht ein mit Trimethylsilan modifiziertes Polyethylenimin als Härter enthält.
8. Ein wärmeempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, daß** die Deckschicht 2-Methylimidazol als Härter enthält.
- 30 9. Ein wärmeempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, daß** die Deckschicht ein Aminoalkyltrialkoxysilan als Kuppler enthält.
10. Ein durch die nachstehenden Schritte gekennzeichnetes Verfahren zur Herstellung einer lithografischen Druckplatte :
 - bildmäßige Belichtung mit Infrarotstrahlung eines wärmeempfindlichen Bilderzeugungselements nach einem der Ansprüche 1 bis 9 und
 - Entwicklung des bildmäßig belichteten wärmeempfindlichen Bilderzeugungselements mit einem wäßrig-alkalischen Entwickler, wobei die belichteten Bereiche der ersten Schicht und der Deckschicht, die ein und dieselbe Schicht sein können, gelöst und die unbelichteten Bereiche der ersten Schicht nicht gelöst werden.

Revendications

- 40 1. Élément de formation d'image thermosensible pour fabriquer un cliché d'impression lithographique comprenant, sur une base lithographique munie d'une surface hydrophile, une première couche englobant un polymère soluble dans une solution aqueuse-alkaline et une couche de protection sur le même côté de la base lithographique que celui sur lequel est disposée la première couche, ladite couche de protection étant sensible au rayonnement infrarouge et étant impénétrable pour un révélateur alcalin, dans lequel ladite première couche et ladite couche de protection peuvent représenter une seule et même couche, **caractérisé en ce que** ladite couche de protection contient au moins un composé contenant des unités époxy en une quantité entre 20 et 500 mg/m² et un durcisseur.
- 45 2. Élément de formation d'image thermosensible selon la revendication 1, dans lequel ledit composé contenant des unités époxy est un produit de condensation d'épichlorhydrine et de Bisphénol A.
- 50 3. Élément de formation d'image thermosensible selon la revendication 1, dans lequel ledit composé contenant des unités époxy est un produit choisi parmi le groupe constitué par des résines de novolaque de o-crésol époxydées et des résines époxy modifiées avec un groupe uréthane.
- 55 4. Élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 3, dans lequel ladite couche de protection comprend une amine à faible viscosité à titre de durcisseur.
5. Élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 3, dans lequel ladite

couche de protection comprend un composé choisi parmi le groupe constitué par des polyaminoamides et des polyamides à titre de durcisseur.

5 6. Élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 3, dans lequel ladite couche de protection comprend un composé choisi parmi le groupe comprenant des monoamines polyoxyalkylénamines, des diamines polyoxyalkylénamines et des triamines polyoxyalkylénamines.

10 7. Élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 3, dans lequel ladite couche de protection comprend une polyéthylèneimine modifiée avec du triméthylsilane, à titre de durcisseur.

8. Élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 4, dans lequel ladite couche de protection comprend du 2-méthylimidazole à titre de durcisseur.

15 9. Élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 8, dans lequel ladite couche de protection comprend un aminoalkyltrialcoxysilane à titre d'agent de couplage.

10. Procédé pour fabriquer un cliché d'impression lithographique, comprenant les étapes consistant à

20 a) exposer en forme d'image à un rayonnement infrarouge un élément de formation d'image thermosensible selon l'une quelconque des revendications 1 à 9 ;

b) développer ledit élément de formation d'image thermosensible avec un révélateur aqueux-alcalin, si bien que les zones exposées de la première couche et de la couche de protection, qui peuvent être identiques, sont dissoutes et les zones non exposées de la première couche restent non dissoutes.

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